

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number:

**0 424 556 A1**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: 89119719.6

(51) Int. Cl.<sup>5</sup>: **C08L 77/06, //(C08L77/06,  
77:06,C08K7:14)**

(22) Date of filing: 24.10.89

(43) Date of publication of application:  
02.05.91 Bulletin 91/18

(54) Designated Contracting States:  
**DE FR GB IT**

(71) Applicant: **MITSUBISHI GAS CHEMICAL  
COMPANY, INC.**  
5-2, Marunouchi 2-chome Chiyoda-Ku  
Tokyo, 100(JP)

(72) Inventor: **Nomura, Isao**  
1001-9, Nakahara Shimojuku  
Hiratsuka-shi Kanagawa-ken(JP)  
Inventor: **Yamamiya, Kazuo**  
7-6, Shimomachiya 3-chome  
Chigasaki-shi Kanagawa-ken(JP)

(74) Representative: **Kraus, Walter, Dr. et al**  
**Patentanwälte Kraus, Weisert & Partner**  
Thomas-Wimmer-Ring 15  
W-8000 München 22(DE)

(54) **Molding polyamide resin composition.**

(57) A molding polyamide resin composition comprising

(A) 50 to 99 parts by weight of a polyamide resin derived from xylylenediamine as a main diamine component and an alpha,omega-straight chain aliphatic dicarboxylic acid as a main dicarboxylic acid component,

(B) 1 to 50 parts by weight of polyhexamethylenedipamide resin,

(C) 5 to 85 parts by weight, per 100 parts by weight of components (A) and (B) combined, of a thermosetting resin powder having an average particle diameter of 1 to 800 micrometers, and

(D) 5 to 200 parts by weight, per 100 parts by weight of components (A) and (B) combined, of glass fibers, the total amount of the polyamide resin components (A) and (B) being 100 parts by weight.

**EP 0 424 556 A1**

This invention relates to a molding polyamide resin composition. More specifically, it relates to a molding polyamide resin composition which has excellent strength at high temperatures, heat aging resistance, mechanical properties, electrical properties and dimensional stability and low water absorption.

A polyamide resin obtained from xylylenediamine and an alpha,omega-straight chain aliphatic dicarboxylic acid (to be abbreviated as "MX nylon") is used as a molding material for various articles because of its excellent mechanical properties, electrical properties, dimensional stability and chemical resistance and low water imbibition. These properties of MX nylon, however, are not sufficient and are unsuitable for practical purposes where it is used as a structural material requiring strength at high temperatures and heat aging resistance in automobile engine covers, silencers, connectors, etc.

Generally, the heating aging resistance of polyamide resins can be enhanced by, for example, adding an antioxidant of the phenol or phosphite type, and the strength at high temperatures of the polyamide resins can be increased by incorporating glass fibers or other inorganic fillers. The additives, however, cannot improve these properties of the MX nylon.

Japanese Laid-Open Patent Publications Nos. 141234/1983 and 152046/1983 disclose resin compositions comprising thermoplastic resins such as polyolefin resins, polystyrene resins, acrylic resins and polyamide resins and granular or powdery phenol-formaldehyde resins. These patent documents cite ordinary nylon 6 and nylon 66 as the polyamide resins, and disclose that by incorporating granular or powdery phenol-formaldehyde resins in these polyamide resins, their heat distortion temperature, volume inherent resistivity upon boiling and compression strength can be improved. A composition comprising an ordinary polyamide resin such as nylon 6 and nylon 66 and a powdery thermosetting resin lacks rigidity when used as a metal substitute, and the improvement of its rigidity is desired.

Heretofore, no practical method of improving the heat aging resistance and strength at high temperatures of a resin composition comprising MX nylon has been known.

It is an object of this invention to provide a novel molding polyamide resin composition.

Another object of this invention is to provide a molding polyamide resin composition having excellent strength at high temperatures, heat aging resistance and thermal resistance.

Other objects of this invention along with its advantages will become apparent from the following description.

In accordance with this invention, these objects and advantages of the invention are achieved by a molding polyamide resin composition comprising

(A) 50 to 99 parts by weight of a polyamide resin derived from xylylenediamine as a main diamine component and an alpha,omega-straight chain aliphatic dicarboxylic acid as a main dicarboxylic acid component,

(B) 1 to 50 parts by weight of polyhexamethylene-adipamide resin,

(C) 5 to 85 parts by weight, per 100 parts by weight of components (A) and (B) combined, of a thermosetting resin powder having an average particle diameter of 1 to 800 micrometers, and

(D) 5 to 200 parts by weight, per 100 parts by weight of components (A) and (B) combined, of glass fibers, the total amount of components (A) and (B) being 100 parts by weight.

The polyamide resins used in this invention are the polyamide resin (A) derived from a xylylenediamine as a main diamine component and an alpha,omega-straight chain aliphatic dicarboxylic acid as a main dicarboxylic acid component and the poly(hexamethylene adipamide) resin (B).

The polyamide resin (A) contains xylylenediamine as a main diamine component. The xylylenediamine may be m-xylylenediamine, p-xylylenediamine, or a mixture of both. Preferred as the xylylenediamine are m-xylylenediamine and a mixture of p- and m-xylylenediamines containing not more than 40 % of p-xylylenediamine. Preferably, the xylylenediamine accounts for at least 85 mole %, especially at least 90 mole %, above all at least 95 mole %, of the entire diamine components.

Other diamines that can be used include, for example, tetramethylenediamine, octamethylenediamine, p-phenylenediamine, 1,3-bisaminomethylcyclohexane and isophoronediamine.

The dicarboxylic acid component of the polyamide resin (A) is composed mainly of the alpha,omega-straight chain aliphatic dicarboxylic acid. Preferably, the alpha,omega-straight chain aliphatic dicarboxylic acid has 6 to 18 carbon atoms. Examples include adipic acid, sebacic acid, suberic acid, undecanoic acid, dodecanedioic acid and eicosanedioic acid. Of these, adipic acid and sebacic acid are particularly preferred.

The amount of the alpha,omega-straight chain aliphatic dicarboxylic acid is preferably at least 85 mole %, more preferably at least 90 mole %, and especially preferably at least 95 mole %, of the entire dicarboxylic acid components.

The other polyamide resin (B) is poly(hexamethylene adipamide) resin (to be sometimes referred to as nylon 66). The nylon 66 can drastically shorten the molding cycle time of the MX nylon.

The polyamide resin (A) is used in an amount of 50 to 99 parts by weight, and the nylon 66 (B), in an amount of 1 to 50 parts by weight, provided that the total amount of the polyamide resins (A) and (B) is 100 parts by weight.

amount of 1 to 50 parts by weight, provided that the total amount of the polyamide resins (A) and (B) combined is 70 to 95 parts by weight.

If the proportion of nylon 66 is less than 1 part by weight as against 99 parts by weight of the MX nylon. If nylon 66 is added in an amount of more than 50 parts by weight per 50 parts by weight of MX nylon, the mechanical strength and rigidity of the resulting composition are degraded.

Preferably, 70 to 95 parts by weight of the polyamide resin (A) and 5 to 30 parts by weight of nylon 66 are combined.

Preferably, 70 to 95 parts by weight of the polyamide resin (A) and 5 to 30 parts by weight of nylon 66 (B) are used to make up 100 parts by weight of the polyamide resins (A) and (B) combined.

Another component used in the composition of the thermosetting resins is a hardener, which is a compound having an average particle diameter of 1 to 800 micrometers. Examples of the thermosetting resin are phenolic resins, xylene resins, melamine resins, epoxy resins, unsaturated polyester resin, urea resins, furan resins, and alkyd resins. These thermosetting resins are preferably used in combination with a hardener. The phenolic resins preferably

Preferred as these thermosetting resins are phenolic resins, xylene resins, melamine resins and epoxy resins. The phenolic resins and xylene resins are particularly preferred. The phenolic resins preferably contain methylol groups, particularly 0.5 to 10 % by weight of methylol groups.

The phenolic resins and xylene resins are particularly preferred as thermosetting resin powders. The phenolic resins contain methylol groups, particularly 0.5 to 10 % by weight of methylol groups.

The average particle diameter of the thermosetting resin powder used in this invention is 1 to 800 micrometers, preferably 1 to 100 micrometers, particularly preferably 5 to 50 micrometers.

If the average particle diameter of the thermosetting resin powder (C) is more than 800 micrometers, the moldability of the resulting composition is reduced.

the moldability of the resulting composition may be produced by the methods described, for

20 the thermosetting resin powder used in this invention may be produced by the methods described, for

Patent Publication No.141234/1983.

[illegible]

The phenolic resin powder used in this invention may, for example, in Referential Example 2 of Japanese Laid-Opdn Patent Publication No.141234/1983.

The xylene resin may be produced, for example, by the following method. Phenol (200 g), 30 g of xylene resin powder (Nikanol H, a tradename for a product of Mitsubishi Gas Chemical Co., Inc.) and 0.1 g of p-toluene sulfonic acid dissolved in a small amount of methanol are introduced into a 1-liter separable flask equipped with a reflux condenser, a thermometer and a stirrer. The temperature is elevated to 100 °C, and the reaction is carried out under reflux for 30 minutes. The reaction mixture is cooled to 60 °C, and 190 g of formalin (37% aqueous solution), 95 g of water, 4 g of 28 % aqueous ammonia, and 40 g of 10 % aqueous solution of gum arabic were added. The temperature is elevated to 87 °C over 40 minutes, and the reaction is carried out at 87 °C for 85 minutes. Then, the reaction mixture is cooled to 30 °C. Water (500 cc) is added, and the mixture is filtered, and dried. As required, the product is sieved to obtain bead-like xylene phenol-resol resin having a particle diameter of 1 to 800 micrometers.

The xylene resin powder can be produced, for example, by the following procedure.

A 500 ml. round-bottomed flask equipped with a reflux condenser and a stirrer is charged with 10 g of melamine, 80 g of benzoguanamine, 170 g of 37 % formalin, 10 g of 25 % aqueous ammonia, 5 g of sodium fluoride, 10 g of calcium chloride and 70 g of water, and with stirring, the materials are reacted at 80 °C for 90 minutes. After cooling, the reaction mixture is subjected to solid-liquid separation. The solid is washed and dried, and as required, sieved to form a non-tacky fine spherical resin powder.

The proportion of the thermosetting resin powder (C) used in this invention is 5 to 85 parts by weight, preferably 10 to 50 parts by weight, per 100 parts by weight of the polyamide resins (A) and (B) combined. If its proportion is less than 5 parts by weight per 100 parts by weight of the polyamide resins (A) and (B) combined, the strength at high temperatures and heat aging resistance of the resulting composition are only insufficiently improved. If it is above 85 parts by weight, the mechanical strength and appearance of articles molded from the resulting composition are undesirably degraded.

insufficiently improved. In this case, the moldability of the composition is undesirably degraded.

45 A further component of the composition of this invention is glass fibers (D). The proportion of the glass fibers (D) is 5 to 300 parts by weight, preferably 10 to 250 parts by weight, per 100 parts by weight of the polyamide resins (A) and (B) combined. If the proportion of the glass fibers (D) is less than 5 parts by weight on the above basis, the effect of this component to improve the mechanical strength and thermal properties of the resulting composition is not sufficient, and if it exceeds 300 parts by weight, the moldability, warping property and surface smoothness of the resulting composition

50 are undesirably degraded.

This resin composition of this invention may be prepared as pellets by melt-kneading at a temperature higher by 5 to 50 °C than the melting

The polyamide resin composition of this invention may be prepared as pellets by melt-kneading components (A), (B), (C) and (D) in an extruder at a temperature higher by 5 to 50 °C than the melting point of the polyamide resins.

The composition of this invention may contain one or more of additives usually employed, for example, stabilizers against oxidation, heat and ultraviolet light, nucleating agents, plasticizers, mold releasing agents, flame retardants, antistatic agents and slip agents. As required, inorganic fillers such as calcium carbonate, talc and wollastonite, whiskers of potassium titanate or silicon carbide, carbon fibers, and alumina silica

ceramic fibers may be incorporated in the polyamide resin composition in amounts which do not impair the objects of this invention.

The polyamide resin composition of this invention has excellent strength at high temperatures and heat-aging resistance, and is useful as automobile engine covers, silencers, connectors, and in other applications requiring heat resistance.

5 The following Examples and Comparative Examples illustrate the present invention more specifically.

The mechanical properties in these examples are tested by the following methods.

Tensile strength: ASTM D638

Tensile elongation: ASTM D638

10 Tensile modulus: ASTM D638

Flexural strength: ASTM D790

Flexural modulus: ASTM D790

#### EXAMPLE 1

15

Forty parts by weight of pellets of poly(m-xylylene adipamide), nylon MXD6 hereinafter, produced by Mitsubishi Gas Chemical Co., Inc. (having a relative viscosity, measured at 25 °C for a solution of 1 g of the polymer in 100 ml of 98 % sulfuric acid, of 2.10), 10 parts by weight of pellets of nylon 66 having a relative viscosity of 2.25, 20 parts by weight of granular phenolic resin (Bell Pearl R-800, a registered trademark for a product of Kanebo Co., Ltd.; primary particle diameter 1 to 20 micrometers), and 30 parts by weight of glass fiber chopped strands with a length of 3 mm were mixed in a tumbler, and the mixture was melt-kneaded at 280 °C in a vent-type extruder, and extruded in string form. The extrudate was cooled over a water bath, cut, and dried to form a molding material as pellets. The material was then injection-molded at a mold temperature of 130 °C to obtain a molded product.

25 The results of the heat-aging test of the molded product are shown in Table 1, and the results of test of its strength at high temperatures are shown in Table 2.

30

#### EXAMPLE 2

A molding material as pellets was produced in the same way as in Example 1 except that 26 parts by weight of nylon MXD6, 10 parts of nylon 66, 14 parts by weight of granular phenolic resin and 50 parts by weight of glass fiber chopped strands were used as the starting materials.

35 The resulting molding material was molded as in Example 1. The results of the heat aging resistance test of the molded product are shown in Table 1, and the results of its strength test at high temperatures, in Table 2.

40

#### COMPARATIVE EXAMPLE 1

45 A molding material as pellets was obtained as in Example 1 except that the granular phenolic resin was not incorporated. The molding material was molded as in Example 1. The results of evaluating the molded product are shown in Tables 1 and 2.

50

#### COMPARATIVE EXAMPLE 2

A molding material as pellets was obtained in the same way as in Example 2 except that the granular phenolic resin was not incorporated, and the proportions of the other components were changed as indicated in Table 1.

55 The molding material was molded as in Example 1 to obtain a molded product.  
The results of evaluation of the molded product are shown in Tables 1 and 2.

COMPARATIVE EXAMPLE 3

Forty parts by weight of pellets of nylon 6 (relative viscosity 2.30), 20 parts by weight of the same  
5 granular phenolic resin as used in Example 1, 30 parts by weight of glass fiber chopped strands having a  
length of 3 mm were mixed in a tumbler. The mixture was melt-kneaded in a vent-type extruder at 260 °C,  
and extruded in string form. The extrudate was cooled over a water bath, cut and dried to produce a  
molding material as pellets.

The molding material was then injection-molded at a mold temperature of 80 °C to obtain a molded  
10 product.

The results of evaluation of the molded product are shown in Tables 1 and 2.

15

20

25

30

35

40

45

50

55

Table 1

Run			Example		comparative Example		
			1	2	1	2	3
Amounts of components (wt. parts)	Nylon-MXD6		40	26	40	26	-
	Nylon-66		10	10	10	10	-
	Nylon-6		-	-	-	-	50
	Phenolic resin		20	14	-	-	20
	Chopped glass strands		30	50	30	50	30
Tensile properties at 23 °C							
Tensile strength (kg/cm <sup>2</sup> )			1710	2000	1900	2650	1690
Tensile elongation (%)			1.3	1.1	1.8	2.0	2.5
Tensile modulus (10 <sup>3</sup> kg/cm <sup>2</sup> )			135	190	130	180	95
Percent retention after aging at 180 °C (*1)	96 hr	Tensile strength	98	104	83	88	95
		Tensile elongation	94	104	94	98	106
		Tensile modulus	105	104	98	100	101
	312 hr	Tensile strength	88	92	67	72	89
		Tensile elongation	90	85	75	76	81
		Tensile modulus	102	104	106	108	102
	576 hr	Tensile strength	80	90	66	70	83
		Tensile elongation	79	82	69	70	65
		Tensile modulus	102	104	106	108	103
	888 hr	Tensile strength	78	87	62	65	77
		Tensile elongation	76	79	60	61	60
		Tensile modulus	102	104	106	108	103
	1152 hr	Tensile strength	76	81	51	54	71
		Tensile elongation	74	75	52	51	53
		Tensile modulus	102	104	106	108	103

(\*) The percent retention after aging at 180 °C for each of the times indicated based on the results obtained by the tensile test at 23 °C.

Table 2

Run			Example		comparative Example		
			1	2	1	2	3
Bending test at 23 °C							
Flexural strength (kg/cm <sup>2</sup> )			2320	3000	2600	3500	2460
Flexural modulus (10 <sup>3</sup> kg/cm <sup>2</sup> )			126	180	100	160	84
Percent retention of hot flexural strength (*2)	50°C	Flexural strength	100	99	100	94	75
		Flexural modulus	98	96	98	96	78
	80°C	Flexural strength	94	81	79	78	44
		Flexural modulus	69	68	62	75	50
	100°C	Flexural strength	72	61	62	52	36
		Flexural modulus	46	47	42	50	45
	120°C	Flexural strength	57	48	52	43	34
		Flexural modulus	42	45	37	43	42
	140°C	Flexural strength	51	40	49	38	33
		Flexural modulus	40	40	36	35	40
	160°C	Flexural strength	42	37	40	35	32
		Flexural modulus	36	35	32	34	38

(\*2): The percent retention of the flexural strength and modulus at each of the temperatures indicated based on the results obtained at 23 °C.

#### Claims

1. A molding polyamide resin composition comprising
  - (A) 50 to 99 parts by weight of a polyamide resin derived from xylylenediamine as a main diamine component and an alpha,omega-straight chain aliphatic dicarboxylic acid as a main dicarboxylic acid component,
  - (B) 1 to 50 parts by weight of polyhexamethylenedipamide resin,
  - (C) 5 to 85 parts by weight, per 100 parts by weight of components (A) and (B) combined, of a thermosetting resin powder having an average particle diameter of 1 to 800 micrometers, and

- (D) 5 to 200 parts by weight, per 100 parts by weight of components (A) and (B) combined, of glass fibers, the total amount of the polyamide resin components (A) and (B) being 100 parts by weight.
2. The composition of claim 1 in which the polyamide resin (A) is derived from a xylylenediamine and an alpha,omega-sraight chain aliphatic dicarboxylic acid.
- 5 3. The composition of claim 2 in which the xylylenediamine is m-xylylenediamine or a mixture of p-and m-xylylenediamines containing not more than 40 % of p-xylylenediamine, and the alpha,omega-straight aliphatic dicarboxylic acid has 6 to 18 carbon atoms.
4. The composition of claim 1 in which the thermosetting resin powder (C) is a powder of a resin selected from phenolic resins, xylene resins, melamine resins and epoxy resins.
- 10 5. The composition of claim 1 in which the thermosetting resin powder (C) has an average particle diameter of 1 to 100 micrometers.
6. The composition of claim 1 in which the amount of the polyamide resin (A) is 70 to 95 parts by weight.
7. The composition of claim 1 in which the amount of the thermosetting resin powder (C) is 10 to 50 parts by weight per 100 parts by weight of the polyamide resin (A) and the poly(hexamethylene adipamide) resin
- 15 (B) combined.
8. The composition of claim 1 in which the amount of the glass fibers (D) is 10 to 50 parts by weight per 100 parts by weight of the polyamide resin (A) and the poly(hexamethylene adipamide) resin (B) combined.

20

25

30

35

40

45

50

55





European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 89 11 9719

DOCUMENTS CONSIDERED TO BE RELEVANT		Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 5)
Category	Citation of document with indication, where appropriate, of relevant passages		
A	EP-A-0 337 443 (MITSUBISHI) * Example 3 *		C 08 L 77/06 // (C 08 L 77/06 C 08 L 77:06 C 08 K 7:14 )
A	--- CHEMICAL ABSTRACTS, vol. 108, no. 10, 7th March 1988, page 48, abstract no. 76543y, Columbus, Ohio, US; & JP-A-62 223 261 (MITSUBISHI GAS CHEMICAL CO., LTD) 01-10-1987		
P,A	--- CHEMICAL ABSTRACTS, vol. 112, no. 16, 16th April 1990, page 59, abstract no. 140645v, Columbus, Ohio, US; & JP-A-01 272 662 (MITSUBISHI GAS CHEMICAL CO., LTD) 31-10-1989		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 5)
			C 08 L C 08 J C 08 K
The present search report has been drawn up for all claims			Examiner
Place of search		Date of completion of the search	LEROU ALAIN
THE HAGUE		31-05-1990	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			